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PROVISIONAL APPLICATION COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 C.F.R. § 1.53(c).

TITLE: THERMAL SWITCH EMPLOYING CARBON NANOTUBES

Inventor(s)/Applicant(s):

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☒ 23 pages of specification are enclosed.

☒ Small entity status is claimed for this application.

☒ Provisional Filing Fee Amount:
☐ $160, large entity
☒ $ 80, small entity

☒ A check in the amount of $80.00 to cover the filing fee is enclosed.

☒ The Director is hereby authorized to charge any additional fees which may be required in connection with the filing of this ~~provisional~~ application and recording any assignment filed herewith, or credit over-payment, to Account No. 02-4550. A copy of this sheet is enclosed.

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The focus of this work is the use of mixed-scale architectures to bridge scales from nanometer level structures to micrometer level components to millimeter level devices and materials. We propose to incorporate carbon nanotubes into microscale composites to create a new kind of mesoscale device, a thermal switch. Arrays of thermal switches will then be produced in batch to create sheets with spatially and temporally controllable "digital" thermal conductivity.

Intellectual Merit of the Proposed Activity

Mixed-scale architectures can be used to bridge scales from nm to μm to mm in order to manufacture materials and devices whose pertinent dimensions range from nanoscale to microscale to mesoscale. Carbon nanotubes (CNT's) are inherently one-dimensional mixed-scale structures, with diameters in the range of nm and lengths in the range of μm. We take advantage of this 10^3 aspect ratio to bring superior thermal and mechanical properties (due to the CNT's nanometer scale diameters), to micro-scale components (making use of the CNT's micrometer scale lengths). Many microelectromechanical systems (MEMS) are also inherently two-dimensional mixed-scale structures with thicknesses in the range of μm and planar dimensions in the range of mm. We take advantage of this 10^3 aspect ratio, to bring the superior thermal and mechanical properties of the micro-scale components to effective use on the meso-scale.

A detailed understanding of structures, properties and functions on the nanometer scale, the micrometer scale and the millimeter scale are required in order to successfully bridge scales from nano-scale structures to meso-scale devices. Indeed, since nanometer structures will affect micrometer scale properties and millimeter scale functions, the understanding sought on each scale will be significantly affected by the other scales. For these reasons, in order to support the manufacturing effort, we propose a program of characterization and modeling that will focus on the nanometer and micrometer length scales.

Carbon nanotubes will be synthesized and then extensively characterized. The nanoscale thermal and mechanical properties of the CNT's will be modeled. The CNT's will then be assembled into aligned arrays within a matrix and formed into micron scale blocks. The thermal and mechanical properties of the aligned CNT composite blocks will then be characterized and modeled. Finally, the CNT composite blocks will be utilized to fabricate prototypes of thermal switch devices.

CNT production, characterization, and modeling along with CNT composite characterization and modeling will be tightly coupled together. Information about structure, properties and function at the nanometer scale will be combined and compared with similar information gathered at the micrometer scale and used to guide both the production of CNT's and their incorporation into the mesoscale thermal switch.

Broader Impact of the Proposed Activity

This proposal will form strong interactions between a large, rural research institution and two urban campuses, making it easier for students from a wide range of demographics to participate in cutting edge research projects. Instrumentation for characterizing thermo-mechanical responses of nanotube assemblies will be created, allowing future work to proceed in these areas. High school teachers from the Northwest will be able to get hand on, practical tools to bring nanotechnology back to their schools, helping to motivate future generations of scientists and engineers. Research on this project will closely couple undergraduates and graduate students, helping to foster integrating research into all levels of education, particularly in groups traditionally under-represented from science and engineering. Overall, this project should help to provide a stimulus to the region for creating meso-scale devices from nano-scale structures, bringing nanotechnology from isolated research labs, to a larger audience, to commercial applications.

This proposal addresses two of the seven research and education themes: first the theme of Manufacturing Processes at the Nanoscale and second issues relevant to Multiscale Multi-phenomena Theory, Modeling and Simulation at the Nanoscale.

INTRODUCTION

The focus of this project is the use of carbon nanotubes (CNT's) to bridge scales from nanometers to micrometers, and MEMS techniques to bridge scales from micrometers to millimeters. Manufacturing across six orders of length scales from nano to meso is made possible by utilizing the mixed-scale architectures of high aspect ratio CNT's (nm diameters to μm lengths) and two-dimensional lithographic-based low-aspect ratio MEMS fabrication techniques (μm thicknesses to mm planar dimensions). By tailoring the length scale of our fabricated structures to the specific functions required, we believe we can achieve superior properties and outstanding device/material performance.

Specifically, we first take advantage of the nanometer-scale diameter of CNT's and their consequently exceptional thermal (thermal conductivity) and mechanical (strength) properties. We then propose to fabricate our aligned CNT composite blocks to the same scale as the micrometer length of the CNT's. By fabricating composite blocks in which each of the individual CNT's stretch across the entire block we expect to see the very large thermal conductivity measured for individual CNT's reflected in a very high overall thermal conductivity for the aligned CNT composite blocks. Finally, by utilizing lithographically-based MEMS fabrication techniques, we propose to manufacture meso-scale devices/materials with spatially and temporally controllable "digital" thermal conductivity. Individual CNT composite blocks will be distributed across a silicon wafer, and aligned opposite an array of thin membranes. Making and breaking contact between the high thermal conductivity CNT composite blocks will enable the thermal conductivity through the device to be changed and controlled at will.

BACKGROUND

The ability to control heat transfer on small time and length scales would have a significant impact in many areas. For example, in just three applications: thermoelectric micro-coolers, DNA amplification via Polymerase Chain Reaction (PCR) and harvesting waste heat to do work on the microscale, these thermal switches would immediately improve the performance of these devices. First, it has been demonstrated that the performance of thermoelectric coolers could be nearly doubled if operated in a transient or pulsed mode [1, 2]. Second, DNA amplification via PCR requires precise temperature control over predetermined thermal protocols as the reactants are cycled through denaturation, extension and annealing temperature regimes. The use of small sample sizes (~ 1 μl) and microfluidic devices has already dramatically reduced both the size and power needs of the equipment needed and the time required for DNA amplification [3-6]. Third, using waste heat to do mechanical work on the micro scale can be accomplished by controlling the flow of waste heat. For example, our group at Washington State University, Pullman (WSU/P) has demonstrated a MEMS-based micro heat engine that can harvest low-temperature heat to do mechanical work and produce electrical power [7]. However, crucial to the operation of the micro heat engine is the means to control the flow of heat into, and out of the engine at very short time scales.

To be able to control heat transfer to thermoelectric coolers, micromachined PCR devices and micro heat engines a type of thermal switch or thermal valve is required. Such a thermal switch would be able to change its effective thermal conductivity in order to turn heat transfer on and off. A first generation prototype of such a thermal switch recently fabricated by our group at WSU/P is described in [8]. The prototype thermal switch consists of a silicon wafer on which is deposited via selective vapor deposition an array of liquid-metal 30 μm diameter micro droplets. A 2 μm thick membrane etched into second silicon wafer positioned above the droplet array is actuated to make and break contact with the micro droplet array. When the liquid-metal droplets are squeezed between the lower wafer and upper membrane, heat is conducted through the thermal switch. When contact is

broken, heat transfer across the gap drops by nearly a factor of ten [9]. With superior materials and optimized design this ratio of effective conductive on to effective conductivity off could be increased by orders of magnitude.

Since the prototype thermal switch is fabricated via standard MEMS techniques, the design is amenable to batch manufacturing. As a result, we are now in the process of fabricating many such thermal switches in arrays that cover an entire wafer. In this way, produced in parallel, the thermal switch arrays will form sheets of material whose effective thermal conductivity can be varied with time and/or spatially across the surface of the sheet. In essence, the sheet of thermal switches will demonstrate a digital thermal conductivity, in which each of the individual thermal element's thermal conductance can be turned up or down at will.

While our first-generation device has demonstrated the basic concept behind the thermal switch, the device is inherently limited by the thermal and mechanical properties of the liquid-metal micro droplets. In particular the relatively low thermal conductivity and the moderate melting and boiling points of the liquid Hg ($k \sim 8$ W/mK) presently used, limits the effective conductance of the "on" thermal switch, the ratio of "on" to "off" conductance and the useful temperature range of the device. Replacing the liquid Hg with a compliant solid material possessing a higher thermal conductivity would greatly enhance the performance of the device. For these reasons a thermal switch employing carbon nanotubes would offer the potential for far superior performance.

Individual carbon nanotubes have been shown to have extremely high heat transfer capabilities. The thermal conductivity of individual multiwalled carbon nanotubes has been measured at over 3000 W/mK at room temperature [10].

However the thermal conductivity of CNT's in aggregate has been found to be disappointingly low. For example, the room temperature thermal conductivity of mats of single-walled CNT's and multi-walled CNT's were measured to be only 35 W/mK [11] and be 25 W/mK [12] respectively. The thermal conductivities of mats of aligned CNT's are somewhat higher with measurements of 60 W/mK found for some samples [13]. Motivated by a desire to create materials for thermal management of microelectronics, efforts have been made to create composite materials by incorporating CNT's into epoxy and polymer matrices [14]. Significant efforts have been made to align the CNT's within the composite materials in order to realize high thermal conductivities [15]. However, the thermal conductivities of these composites while higher than the matrices are still significantly lower than had been hoped.

The commonly assumed reason for the low thermal conductivities of aggregate CNT's whether in mats, or in composite form, is the poor thermal coupling (or high thermal resistance) between CNT's [16]. Under this hypothesis, while the thermal resistance of individual CNT's is extremely low, the thermal properties of the aggregate is dominated by thermal transport from one CNT to the next in the mat or composite. Based on this hypothesis, one possible route to successfully exploit the extremely high thermal conductivity of individual CNT's to create structures with exceptional thermal properties is to match the length scale of those structures to the length scale of the CNT's.

For these reasons, we propose to match length scales with the CNT's by fabricating PMMA/CNT composite blocks with thicknesses comparable to the lengths of our CNT's, on the order of 10 μm. In these micro-scale composite blocks, the CNT's incorporated into the matrix will on average span the entire thickness of the blocks. ~~Under these conditions, heat~~ will be transferred along uninterrupted CNT paths, with no high resistance bottlenecks between CNT's. We thus intend to use the high aspect ratio CNT's to bridge from the nanoscale to the microscale, creating CNT composite bridges with thermal and mechanical properties superior to monolithic materials.

We will then use MEMS fabrication techniques to distribute these PMMA/CNT composite blocks to realize arrays of thermal switches. The arrays of thermal switches will in turn serve as the basis for our digital thermal sheets.

RESEARCH OBJECTIVES

The objective of this project is to manufacture a device with a digital thermal conductivity that can be controlled with high resolution both temporally and spatially.

To achieve this objective several major tasks are required:

1. Synthesis of individual CNT's in soot form and oriented CNT's on templates as shown in Fig. 1a.
2. Characterization of CNT structures (length, diameter, chirality, single vs. multi walled, and presence of defects) and chemistry.
3. Characterization of CNT properties (thermal conductivity, elastic modulus, strength).
4. Fabrication of composite blocks consisting of aligned arrays of CNT's within a PMMA matrix as shown in Fig. 1b and aligned CNT arrays with matrix removed as shown in Fig. 1c.
5. Characterization of composite block structures (CNT orientation, CNT density, CNT connectivity).
6. Characterization of composite block properties (thermal conductivity, elastic compliance, strength).
7. Modeling thermal and mechanical properties of individual CNT's using molecular dynamics.
8. Modeling mechanical response of aligned CNT's and CNT composite block structures using continuum methods.
9. Design and fabrication iteration of a device based on the results of the above tasks.

a b c

Figure 1. Nanotube structures proposed to measure and control heat transfer. CNT's synthesized using FIB (a), composite blocks of CNT's (b), and blocks of CNT's with matrix removed (c).

RESEARCH PLAN

To achieve the goal outlined above we have assembled an interdisciplinary team of faculty from mechanical engineering, manufacturing engineering, physics, electrical engineering, and materials science. There are three institutions involved: Washington State University Pullman, WSU/P; Washington State University Vancouver, WSU/V; and Portland State University, PSU. The experimental and modeling plans are described below.

EXPERIMENTAL PLAN

Synthesis and characterization of individual Carbon Nanotubes

Individual CNT's in soot form will be synthesized using a CVD system, modified to apply controlled magnetic and electrical fields. The CVD system will be used to investigate the effects of preparation conditions on the formation of different morphologies of CNT's. The role of each parameter responsible for the geometrical configuration of nanotubes will be identified and conditions optimized for growing CNT's of designed specifications. This effort will focus on synthesizing high yield powder samples of high purity single-walled and multi-walled CNT's. Fig. 2 (a) and (b) are the HRTEM images of single-walled and multi-walled nanotubes, respectively synthesized at PSU these samples in the form of soot macroscopically. In this proposed research the CVD reactor will be modified to study the effect of magnetic fields and electrical fields on the formation of nanotubes, and

in particular on the growth orientation of the tubes. This will be accomplished by setting up a system that can provide either a magnetic field or an electrical field to the region of nanotube growth. Nanotube samples will be produced with several variations of magnetic and electrical fields; samples will also be produced without the effects of these fields.

A matrix of possible combinations of preparation parameters has been developed including the type of catalyst (Fe, Co, and Ni), type of hydrocarbon gas (C_2H_2, C_2H_4, CH_4,CO), the type of activation gas (H_2, NH_3), the gas flow rates, ambient pressures, reaction temperatures, reaction durations, and magnetic and electric field strengths. The structure and chemistry of CNT's synthesized under each set of parameters will be characterized using SEM, HRTEM and STEM. In particular we will focus on identifying the length, diameter, chirality, single wall versus multi-wall structures, and the presence of defects in the CNT's. Additionally, the structure and incorporation of catalyst materials in the CNT's in soot form will be identified.

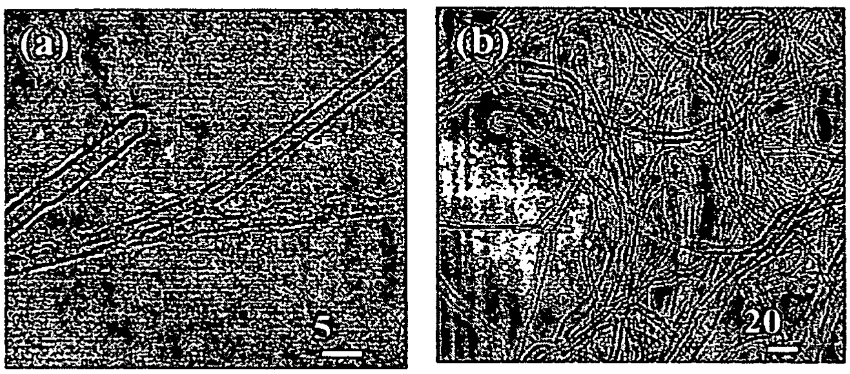

Fig. 2 (a) and (b) show the high-resolution TEM images of single-walled and multi-walled nanotubes, respectively. These samples were produced by Prof. Jiao's group at PSU.

A characterization of individual tube properties, particularly the thermal conductivity, elastic modulus, and strength, of the CNT's synthesized at PSU will be performed by WSU/V. Since the CNT's may be synthesized with different morphologies under various forming conditions, a systematic evaluation of the nanotube physical properties is required to address the dependence of the mechanical and thermal properties of nanotubes upon the atomic structure under various forming conditions.

A scanning probe microscope at WSU/V will be used to measure the atomic structure and dimension of both SWNT and MWNT[17,18]. The presence of structural defects, the chirality and the tube diameter of CNT's manufactured using different synthesizing conditions will be obtained. Initial images of CNT's taken by STM and AFM are shown in Fig. 3.

We can modify the AFM into a scanning thermal microscope which will be able to provide measurement of the sample surface temperature based on reports in the literature [19]. A micro thermocouple will be fabricated to serve as the scanning thermal probe. Measurement of the elastic properties at low strains (Young's modulus) of individual CNT's will be measured using AFM [20]. The CNT's that are suspended across gaps or holes of substrate may be deflected using AFM force curve methods. The force exerted on the tubes by AFM tip is recorded simultaneously with the imposed deflection, and the Young's modulus of nanotube can be extracted if

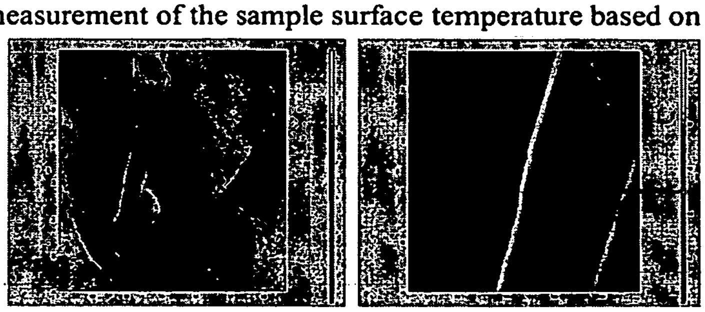

Fig. 3 CNT's imaged using STM. Image on left is 1.4 μm square; image on right is 250 nm square.

the cross sectional size is known and the assumption of a clamped beam is made. We will also attempt to use AFM to find the maximum strain at which non-elastic behavior of the nanotubes initiates [20,21], but do realize that applying strains to these levels with AFM methods may be beyond the current instrumentation capabilities.

These data will form a data base which can be used to correlate mechanical and thermal properties to CNT synthesis conditions. These results will be used by PSU to help define optimal synthesis conditions and used by WSU/P for incorporation in both the modeling and testing of composite blocks and assemblies of CNT's.

Growth and Characterization of Templated Arrays of CNT's

Synthesis of oriented CNT's on templates will be accomplished through two routes. First, focused ion beams will be used to deposit templates of iron on which CNT's will grow. Secondly, methods of self patterning via heat treatment to form nanoclusters of iron and nickel will be done through thermal decomposition.

There have been many published reports of methods of achieving highly textured nanotube structures in the literature. Many of the methods are based on growing aligned structures. These include growing on templated nickel nanodots after patterning using e-beam lithography [22], or more bulk methods such as spinning solutions of nanopowders onto substrates for complete coverage and growth of larger area films [23]. It is also possible to spin coat substrates with organometallic compounds, and then through subsequent heat treatment cause nanoscale metallic or oxide catalyst structures to form [24]. The nature of aligning the nanotubes is related to both the density of sites which initiate tubes (with catalytic materials) and the direction of the applied electric field from the plasma during PECVD growth.

The first route to synthesize templated nanotube structures will be carried out utilizing a focused ion beam system equipped with a gas injection apparatus. The catalyst will be deposited on designated locations by ion beam induced metal deposition of a gaseous compound via the capillary needle-sized nozzle of the gas-injection apparatus. The substrate containing patterned catalysts will then be moved into the CVD reactor and optimized parameters will be used for tube growth. have recently used this approach to create patterned Fe catalyst clusters on the silicon substrate by focused ion beam induced decomposition of ferrocene [$Fe(C_5H_5)_2$]. When these processed substrates were put in the CVD reactor, CNT's were formed in a patterned configuration. Fig. 4 shows that the growth of CNT's was confined within a cluster of Fe catalysts. Fig. 5 demonstrates that nanotubes formed in a pattern of columns where catalyst particles were first deposited in the form of columnar structures by

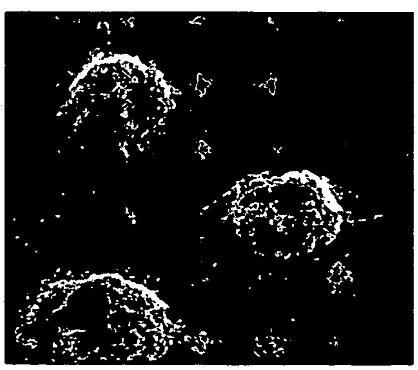

Fig. 4: Nanotubes grown out of Fe clusters generated by FIB decomposition of Ferrocene. The CNT's are multi-walled.

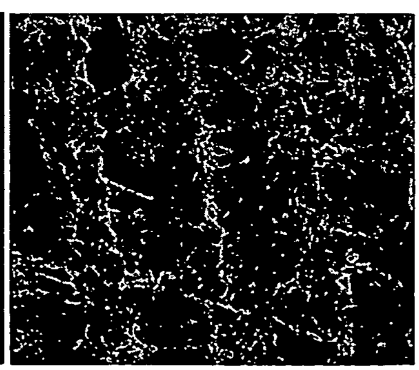

Fig. 5: Nanotubes formed in a pattern of columns generated with the FIB system.

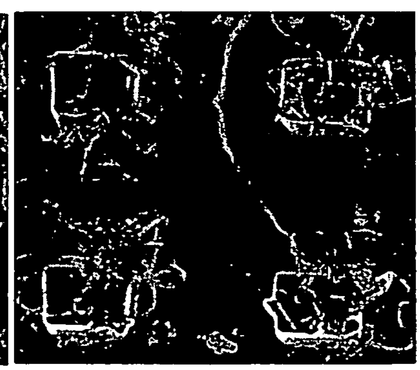

Fig. 6: Nanotubes formed directly from the top of Pt pillars produced with our FIB and CVD systems.

the FIB and then nanotube growth was achieved in the CVD reactor. We have also synthesized CNT's directly on the top of the electrodes as shown in Fig. 6. Although these results are not perfect, they demonstrate the feasibility of this combination of the FIB and CVD processes, and encourage further development of this fabrication technique. The second route to synthesize templated structures involves spin coating iron nitrate solutions onto silicon wafers, and subsequent heat treatment to form arrays of iron and iron oxide nanoparticles over entire substrates in batch form.

Fabrication of CNT Composite Blocks

Composite blocks consisting of aligned arrays of CNT's within a matrix, as shown in Fig. 1b and aligned CNT arrays with matrix removed as shown in Fig. 1c will be fabricated. Several research groups have demonstrated the ability to align carbon nanotubes in polymers through a combination of composite processing methods. Sennett et. al. [25] has shown that by mixing nanotubes with thermoplastic polymers (polycarbonate) it is possible to align tubes into composite fibers 0.5 mm in diameter. Other polymer matrix materials, such as polystyrene, can be treated in a similar manner, producing either thin fibers with a aligned composite or a randomly oriented film after casting [26]. It is also possible to demonstrate thermoplastic polymer - nanotube composites with spin coating, such as the case of nanotube - poly methyl methacrylate (PMMA) composites which demonstrate a percolation threshold at 0.5 volume percent, and a change from semiconducting to metallic electrical behavior at this loading [27]. Similarly, thermosets can be used to form composites which show connectivity and a percolation threshold at very low loadings [28].

In this project we will fabricate nanotube - polymer composites to develop aligned structures for thermal management. First, spin coating thin films (1 -4 μm) with loadings of about 1-10% will provide structures with relatively isolated but aligned tubes [27]. Repeated spinning and annealing will be carried out until the total film thickness reaches 100 μm. At this point, a thick capping layer of PMMA will be spun to cap the structure. The samples will be cross sectioned using standard polishing techniques for sample preparation for transmission electron microscopy, and then core drilled and polished to create 3 mm discs with a 5 - 50 μm layer of aligned composite, as shown in schematically in Fig. 7. In this thin section of material, the CNT's will bridge the entire nanocomposite leading, we believe, to exceptional thermal and mechanical properties.

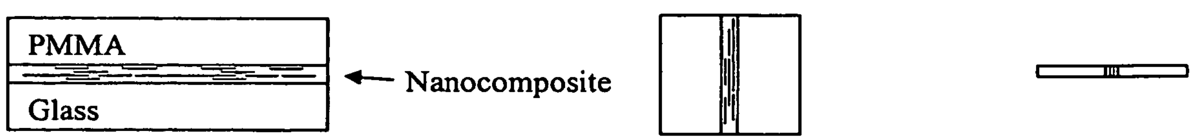

Figure 7. Process steps for spinning, sectioning, and polishing samples of PMMA - nanotube composites to measure thermal properties of aligned composites. From spinning (left) to sectioning (middle) to thinning (right), the nanotube structures will be isolated for thermal transport and mechanical property measurements.

Once these blocks have been fabricated, the PMMA can be removed through chemical dissolution. However, this would cause the CNT's to form a mat structure, rather than the aligned pattern shown in Fig. 1c. Therefore, a metallization layer (sputtered and or electroplated Au and Ni) will be used to cap the CNT block structure. Then, upon exposure to acetone or other organics which dissolve PMMA, we will be left with the array structure shown in Fig. 1c.

Characterization of CNT Composite Blocks

Characterization of composite block structures (CNT orientation, CNT density, CNTS connectivity) will be carried out using the SEM and TEM facilities available at WSU/P. Characterization of composite block properties, such as thermal conductivity, elastic compliance, and strength, will be carried out using a novel device to be developed in house at WSU/P. We will construct and assemble a device based on the vacuum - compatible load transducer produced by Hysitron, Inc. The system will be capable of applying loads between 0.1 and 100 mN. A schematic of the system is shown in Fig. 8. The system is designed such that ambient air, inert gasses, or a vacuum of approximately 0.1 mTorr can be achieved in the chamber.

The transducer and the digital microscope will be calibrated a fixed distance apart. This enables the region of the sample to be positioned to within 0.1 mm. The XYZ stage will be used to translate the sample from the microscope to the transducer, with the axis controlled by commercially available positioners. The optical microscope will be used to note the position of the nanotube clusters, and provide a reference to other fiduciary marks on the nanotube samples to determine density of arrays using post-test electron microscopy.

The instrumented base will be similar in design to the test fixture used to measure heat transfer rates across the liquid-metal micro-droplet thermal switch as described in references [8]and [9]. That device consists of a guard-heated calorimeter (GHC) located above the liquid-metal micro-droplet thermal switch and a second resistance thermal detector (RTD) located below the liquid-metal micro-droplet thermal switch. The device has proven very successful, with an accuracy sufficient to measure the heat transfer rates across prototype thermal switches in both "on" and "off" states with an uncertainty of no more than a few percent.

A similar arrangement will be used in the proposed work. In this case the guard-heated calorimeter micromachined on a 2mm square silicon die will be mounted on the Hysitron transducer tip. An RTD micromachined on a second 2mm square silicon die will be mounted on a thermal sink. The thermal sink will in turn be mounted on the piezoelectric XYZ stage. Nanotube and nanotube composite samples will be place on top of the lower RTD die.

The piezoelectric stage will raise the samples into contact with the load cell and micromachined GHC. During this approach stage, the heat transfer through the gas medium will be measured. As the sample makes contact with the micromachined GHC, the piezoelectric stage will stop. At this point, the Hysitron transducer will be used to impose a predetermined loading rate upon the micromachined GHC while monitoring the deflection of the structure. This will provide both the mechanical response of agglomerations of nanotubes as well as allowing heat transfer measurements.

Several significant technical challenges must be overcome to carry out these experiments. However, by selecting the Hysitron Vacuum Transducer as the method of applying load and displacement, we are able to utilize a system which has already been demonstrated to carry out most of these requirements. Previous Hysitron systems for nanoindentation and nanomechanical testing have been instrumented in the indentation tip with acoustic emission sensors. Therefore, attaching the electrical connections to the micromachined GHC is very feasible, in a manner similar to the previous acoustic emission testing fixtures. Secondly, applying mechanical loading in vacuum can be problematic, as the instruments often apply large voltages which can lead to the formation of a plasma and damage the device. Hysitron has already designed a system which is capable of running in vacuum, and therefore we've chosen this commercially available (though custom designed) system to apply loads and monitor displacements with the resolution required for these experiments. Similarly, thermal effects could lead to extensive drift in these tests. This will be controlled in two ways. First, the brass plate near the micromachined GHC will act as a heat sink, but the glass-ceramic rod which is threaded to connect the brass to the transducer will greatly reduce thermal conduction to the transducer. Secondly, the ability of the Hysitron system to carry out testing in a

rapid period of time (less than 1 minute) should minimize thermal drift, and allow relatively little heat to transfer to the transducer structure.

One other technical challenge is the parallel plates between which the test must occur. There will invariably be some angle between the micromachined GHC and the sample. However, by constructing a post structure from electroplated gold, copper, or nickel on the RTD, it will be possible to minimize these effects. The micromachined GHC will be calibrated against a clean area of the sample to adjust the compliance of the system. Then, after compliance calibrations the nanoscale compression testing will be carried out on the actual area of the sample to be examined (and previously located via the optical microscope).

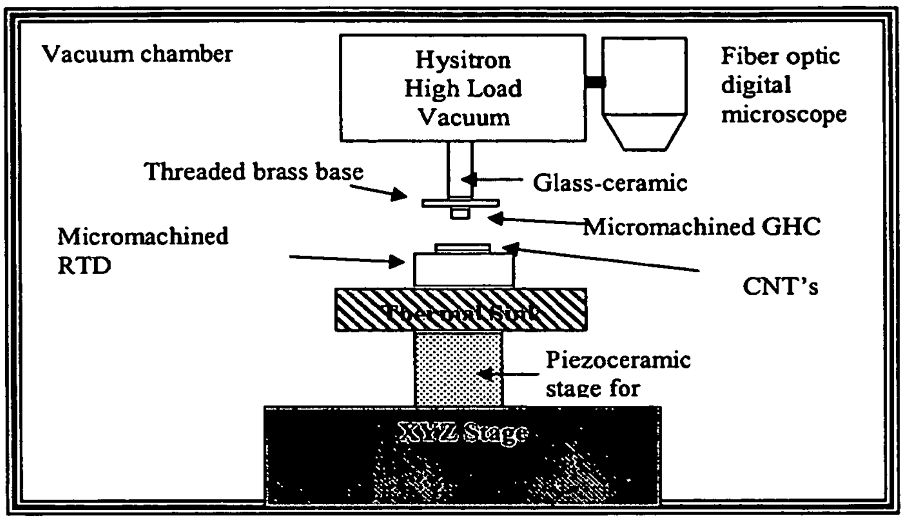

Figure 8. Schematic of vacuum thermal-mechanical properties testing system incorporating commercially available transducers with in-house fabricated MEMS

Developing the testing fixture described in the previous section will require a significant time investment for instrument development and calibration. To verify the basic concept, initial ambient tests will be carried out using the two nanoindentation systems available on the WSU campus. The existing Hysitron Triboscope, which is mounted to a Park CP Scanning Probe Microscope, can be used with a micromachined GHC system to carry out an initial verification of calibrations. WSU and other researchers have already developed and demonstrated the ability to create novel tip geometries, such as the addition of a 60 μm radius of curvature diamond tip, or to carry out experiments in fluids with the sample under electrochemical control [29]. In addition, members of the team have already gained significant experience in the use of a similar micromachined guard-heated calorimeter to make heat transfer measurements on the liquid-metal micro-droplet thermal switch. The initial testing (first 6 months of the project) will use the existing system. Similarly, if the Hysitron system currently on campus (which is only instrumented for loads up to 10 mN) is too small, a similar tip geometry will be added to the existing Nanoinstruments Nanoindenter II. This exact instrument has already been altered to accept heating stages [30] and acoustic emission systems [31], and so it should be feasible to add the thermal measurement capability to this experiment.

MODELING PLAN

Thermal and mechanical properties of individual CNT's will be modeled using molecular dynamic simulations (MD). The mechanical response of aligned CNT's and CNT composite block structures will be modeled using continuum methods.

The successful integration of carbon nanotubes into devices demands understanding how their thermal conductivity is affected by factors such as: (1) bending and stress, (2) inter-nanotube interactions, (3) size and orientation of nanotubes, (4) defect and buckling, and (5) details of the

interface between nanotubes and silicon. The molecular dynamic approach with realistic potentials provides an ideal tool to investigate the thermal properties of individual CNT's. However, modeling the deformation of nanotubes in large assemblies using MD can be computationally expensive [32]. We will take a two tiered approach to modeling. Using MD we will focus on modeling the thermal properties of CNT's and obtaining the mechanical constitutive laws for use in the continuum model. We will use an approach based on continuum mechanics to develop predictive models for bending and buckling behavior of CNT's. This will allow us to extend the computational domain to the length and time scales required to bridge from the nanoscale to the microscale. This is required for the design of practical devices.

The presence of nanotubes of different chiralities (metallic and semiconducting), sizes and orientations in nanotube blocks makes it impossible to predict their overall thermal conductivity using simple analytical approaches. For example, changes in nanotube diameters can excite different radial phonon modes that participate in transmitting heat and phonon-phonon interactions at high temperatures. The weak inter-nanotube coupling, at best similar to the inter-basal plane coupling in graphite, results in lower thermal conductivity. Furthermore, bending and buckling of the nanotubes leads to a decrease in the thermal conductivity. The quasi-one dimensional nature of the carbon nanotubes also makes boundary scattering very important. The electronic contribution to thermal conductivity of carbon nanotubes was shown to be negligible over all temperature ranges [33].

The discontinuity at the interfaces introduces an additional thermal resistance due to the difference in bond length and masses on both sides of the interface. Modeling the interface still remains a challenging problem using atomic level simulations due to the difficulty in defining a suitable empirical potential that accounts for interaction between atoms of different species. One can, however, gain some feel of the interface role by considering only the mass change at the interface. For example, Picket and coworkers investigated the transmission of phonon energy across a model interface where only the atomic masses changed while maintaining a diamond type structure [34].

The goals of the MD simulation are to investigate:

(1) the thermal conductivity of a) straight single wall nanotubes with different diameters and chiralities, and b) straight multiwall nanotubes and nanotube ropes
(2) how mechanical stress and bending affects the thermal conductivity of individual tubes.
(3) the effect of interfaces and defects on heat transfer.

For goal (1) both direct non-equilibrium MD with periodic boundary conditions and the equilibrium MD using Green-Kubo formula will be used and take into account size effects. On the other hand for goals (2) and (3), direct NEMD with non-periodic BC along the tube axis will be used. Additionally, the phonon spectrum will be determined from the velocity autocorrelation function and investigated for any shifts due to bending, stress or interface effects. An additional goal is also to determine a set of rules for predicting the thermal conductivity of carbon nanotube blocks based on the MD results obtained in (1) and (2) and approximate spatial distribution of nanotubes in the mat. The choice of the nanotube parameters such as chirality and diameters will match those grown for this project. Additionally, the temperature range used in the simulations will correspond to those present in the testing of the CNT composite blocks.

The proposed research builds upon the earlier investigations at WSU of the thermal conductivity of (1) straight single wall carbon nanotubes and its dependence on the geometry of the tubes (radius and chirality) [35] and (2) Y-junction nanotubes, and (3) heat pulse propagation in carbon nanotubes using molecular dynamic simulations.

Molecular Dynamic Approach: The MD simulations will use the Tersoff-Brenner bond order potential for the C-C bond as the potential interaction to model the dynamics of the atomic interactions and solve the classical Hamilton's equations of motion with a predictor-corrector algorithm [36,37]. The calculation of thermal conductivity will be done using either the equilibrium MD (EMD) or non-equilibrium MD (NEMD) approaches.

Equilibrium MD Approach: This approach uses current fluctuations to calculate the thermal conductivity λ, via the fluctuation dissipation theorem. The MD approach is used to compute the autocorrelation function of the heat flux, which is related to the thermal conductivity by the Green-Kubo formula given by:

$$\lambda = \frac{V}{k_B T^2} \int_0^\infty \langle J_z(0) J_z(t) \rangle dt$$

T is the system temperature, $J_z(t)$ is the z-component of the heat flux, k_B is the Boltzmann constant, and V is the volume of the sample under investigation. For CNT's, the z-axis is assumed to parallel to the nanotube. The advantage of this approach is that simulations are done under equilibrium conditions at the given temperature without imposing any driving forces such as a temperature gradient or a fictitious force as in the non-equilibrium MD approach. Unfortunately, very long simulation times are required to ensure the convergence of the current-current autocorrelation function. Additionally, this approach is implemented in our MD simulation program and will be used to calculate the thermal conductivity of some of the nanotubes and as calibration tool for the non-equilibrium approach. The use of periodic boundary conditions can lead to size dependence of the thermal conductivity if the simulation region length is shorter than the mean free path of the phonons and lead to underestimation of the thermal conductivity. For example, Che and coworkers [38] have shown that for (10,10) single wall CNT's longer than 20 nm at 300K, the thermal conductivity converged to a constant value.

Non-equilibrium MD Approach: In this case, one can either apply a temperature gradient or introduce a fictitious force term and modify the equations of motion which forces the system out of equilibrium and results in a heat flux to counter the effects of the temperature gradient or the external force [39,40]. Here, the procedure proposed by Oligschleger and Schön[39], and implemented in straight nanotubes by Osman and Srivastava[35], will be used. In this procedure, the CNT is split up into a series of adjacent "slabs" of atoms. Two of the slabs are thermally regulated to enforce a temperature gradient upon the system by a scaling of the velocities of the atoms within the slab to the desired temperature at the end of each time step From the change in energy of the controlled slabs at each time step the heat flux density is determined and time averaged over the simulation times. After a large number of simulation steps, an equilibrium value of the heat flux density is obtained. The temperature gradient is found by applying a linear fit to the temperatures of the slabs, and the thermal conductivity is merely the quotient of these two values. This assumes a Fourier relationship between the thermal conductivity and heat flux to be valid. The choice of temperature profile permits application of periodic boundary conditions along the straight nanotube axis in order to eliminate edge effects [39].

While the procedure appears to be simple, one has to take into account size effects and ensure the length of simulation box is greater than the mean free path of the phonons and that the system remains in the linear response region. In the past we have used the values calculated by EMD to check the consistency of the results and adjusted the length of simulated sample. For bent CNT's and interface simulations, one can not use periodic boundary conditions and the hot and cold slabs are kept near the ends of the CNT.

Continuum Modeling. There is good reason to believe that an approach based on continuum mechanics will allow us to have predictive models for the operating regime of our devices [41]. As an assembly of CNT's is subjected to a load there are three regimes of deformation: linear elastic; non-linear elastic (post-buckling); and inelastic (bond breaking and reforming). The goal of the continuum modeling is to optimize the compliance/conductivity properties of the configuration in Fig. 1(b) and (c). In addition, the transitions between the various deformation regimes (linear, buckled, inelastic) will be predicted to provide design guidelines.

In the linear elastic regime, Yakobson et al. [41] considered bending and compression of single-wall CNT's, and showed that linear stability analysis based on classical elastic shell theory accurately predicts the onset of buckling from uniform deformation. Beyond the linear elastic regime, simulations and experiments for both tension and compression/bending of nanotubes indicate that the nanotubes are still elastic up to very high strains [42, 43, 44], but are no longer simply linear elastic. For example, in tension, elastic behavior is expected up to 5-6% strains [45, 46]. In compression, even after buckling and buckling localization, elastic behavior is expected up to 8-12% strain [47]. Beyond the elastic regime, CNT's exhibit a change of structure. In tension, the hexagonal structure of the graphite sheet changes locally to four pentagons and heptagons (5-7-7-5 defects) by bond rotation [45]. In bending and compression/buckling, the change in coordination occurs from 3-fold (sp^2) to 4-fold (sp^3) [47, 48]

What is still needed for this work is to go beyond the linear regime into the post-buckling regime in a computational method that can treat assemblies of nanotubes (i.e. a continuum approach). We propose to bring the full power of nonlinear shell theory [49,50 51] to the problem.

The configurations to be considered are shown in Fig. 1. The pin-cushion configuration (Fig. 1(a)) results from the initial growth of CNT's. The nanotubes have different orientation and the load on each one will vary from pure compression to predominantly bending. The problem of a CNT composite block in compression (Fig. 1 b)) is relatively simple compared to the other ones for the lateral support of the matrix is expected to prevent buckling of CNT's. When the composite is dissolved, and nanotubes are anchored in metal films (Fig. 1(c)), the resulting configuration is one with "slightly misaligned" CNT's, predominantly in compression. Depending on the misalignment, some nanotubes will bend and locally buckle at small loads, others only at higher loads. The formation of local buckles diminishes thermal conductivity of a nanotube.

The fundamental mechanical problem is a CNT under a combined compressive and transverse force. The interest is in post-buckling deformation. In an assembly such one in Fig. 1(c), a buckled CNT sheds load to other CNT's. With the solution to the fundamental problem, and the statistics of misalignment of CNT, the solution to the problems illustrated in Fig 1(a),(c) can be obtained, and compared to the mechanical testing of the CNT composite structures.

The nonlinear theory of shells has several formulations [49, 50, 51]. The main features are separate nonlinear measures of the membrane strain $\varepsilon_{\alpha\beta}$ and the bending strains $\mu_{\alpha\beta}$. The Greek indices take values 1 and 2, referring to the initial axial and circumferential directions.

In the classical shell theory, the bending measure $\mu_{\alpha\beta}$. refers to the middle surface of the shell and produces liner distribution of strain across the thickness. With thus computed strains, linear elasticity is used to obtain stresses, and then forces N and moments M, by integration of stresses across the thickness. Nanotubes are a special case of shells with no thickness defined and their constitutive properties cannot be deduced from linear elasticity. For now, assume that constitutive relations are given. The principle of virtual work then takes the form

$$\int_A \left(N^{\alpha\beta}\delta\varepsilon_{\alpha\beta} + M^{\alpha\beta}\delta\mu_{\alpha\beta} \right) dA = N\delta U + T\delta V$$

where A is the area of the shell, N and T are normal and transverse force with corresponding displacements U and V. The variational principle given above is the basis for the standard development [52] of the finite element formulation suitable for the problem in hand.

Finite element procedure for analysis of post-buckling behavior of cylindrical shells has been developed by Tvergaard & Needleman [53]. They considered shallow cylindrical panels under compression and established criteria for buckling and buckling localization. The onset of buckling instability is growth of periodic perturbation. Subsequently, the buckling localizes to a single

"pinched" region. The linear stability analysis [41] of nanotubes only predicts the onset of periodic buckling. To describe the post-buckling behavior, the full nonlinear formulation is needed.

In the post-buckling regime, the nanotubes will be elastic until a change of bond coordination occurs. However, this elastic regime will not be linear.

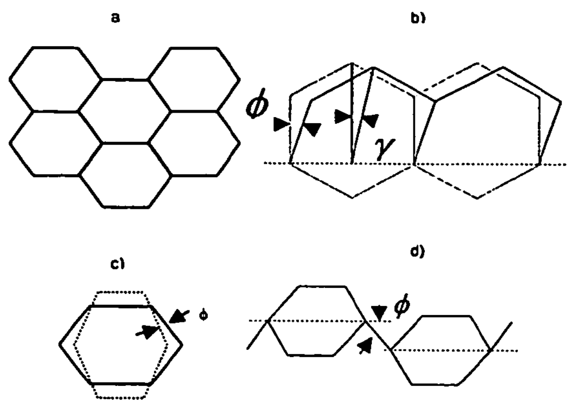

Fig. 9. Schematic of changes in bonding of carbon nanotube structures.

We begin with the in-plane behavior of a graphite sheet. Its hexagonal structure is given in Figure 9(a). The in-plane strains are the result of two elementary processes: bond stretching and the bond angle variation. Stresses now have units of force per unit length. The mean stress $\sigma = (N_{11} + N_{22})/2$ produces only bond stretching, which is small, so that this portion of deformation can be modeled with a linear law: $\varepsilon^{(1)} = \sigma/B$, where B is the analogue of the bulk modulus in 3D elasticity.

The deviatoric (shear) stress, τ is

$$\tau = \sqrt{N_{12}^2 + \left(N_{11} - N_{22}\right)^2/4}$$

and produces a bond angle variation ϕ, which in turn, results in both, change in shape, γ (Fig. 9(b)), and change in area $\varepsilon^{(2)}$ (Fig. 9(c)):

$$\gamma = 2\phi/3$$

$$3\left(2\bar{\varepsilon}^{(2)} + 1\right) = \cos(2\phi) + \cos\phi - \left(\sin(2\phi) - \sin\phi\right)/\sqrt{3}$$

The constant B and the relation $\phi = \phi(\tau)$ are all that is needed to formulate the in-plane nonlinear elastic constitutive law for nanotubes:

$$\bar{\varepsilon} = \bar{\sigma}/B + \bar{\varepsilon}^{(2)}\left[\phi(\tau)\right] \text{ and } \gamma = 2\phi(\tau)/3$$

For small strains this relation will reduce to linear elastic law used by Yakobson et al [41].

The computational configurations to obtain $\phi(\tau)$ and B are periodic (Fig. 9(b), (c)) and are thus amenable to unit cell analysis by MD methods.

Out-of-plane, or bending stiffness, is entirely due to the out-of-plane change of bond angle. (In contrast with solid shells where the bending stiffness is a result of relation between normal stresses and strains.) A periodic unit cell, shown in Fig. 9 (d) can be defined to make MD computations economical.

With the elastic properties thus defined and the nonlinear shell theory at hand, we propose to analyze the onset, development and localization of instabilities in compression/bending problem. This resulting fundamental solution will then be combined with the orientation statistics to model the experimental situations (Fig. 1 (a) and (c)). For the experimental configuration in Fig. 1(b), we expect the standard model for fiber composite to hold.

The last component of modeling is the criterion for the onset of inelastic deformation (change in bond coordination). The criterion will be based ~~on the~~ bond rotations (Fig. 9 (d)). From MD computations, the critical change of angle between the bonds will be determined. For the case of localized buckling, the appropriate continuum measure is the bending strain measure $\mu_{\alpha\beta}$..

DEVICE REALIZATION

Design and fabrication of a device with a digital thermal conductivity that can be controlled with high resolution both temporally and spatially will be based on the results of the preceding work. The mesoscale device will be based on the assembly of micro-scale blocks of the CNT composite. After

spinning, annealing, capping, and sectioning the PMMA/CNT nanocomposite, 300 x 100 x 10 μm strips of the material will be cut and loaded in an aqueous suspension. Two silicon wafers will then be prepared to form the top and bottom of the device as seen in Fig. 10. The top wafer will hold the nanocomposite strips. The bottom wafer will be patterned with an array of membranes and pillars.

First a 3 – 5 μm thick layer of oxide will be thermally grown on the top wafer. A series of Au electrodes and leads will be sputtered on the oxide and patterned lithographically. Next, an array of 300 x 100 mm rectangles will be defined and pits etched into the oxide, down to the Si. These 3 – 5 μm deep, rectangular pits will act to position the nanocomposite strips on the Si wafer. The Si wafer will be flooded with the aqueous suspension of nanocomposite strips and then agitated. As the CNT/PMMA composite strips settle, they should preferentially lodge in the rectangular pits. The remaining liquid of the aqueous suspension will be evaporated, leaving the wafer surface covered with the electrode array and the nanocomposite strips, similar to the manner of aligning optical fibers and other fluidic self assembled structures [54,55].

An array of membranes will be etched into the bottom wafer. First a low temperature thermal oxide will be grown on the bottom wafer. An array of 1400 μm squares will be defined photolithographically and etched to form an oxide mask on the back surface of the Si wafer. An anisotropic wet etch will then be used to create 2 μm thick boron doped Si membranes as defined by the oxide mask. Next, a series of Au electrodes and leads will be sputtered onto the oxide on the front surface of the wafer and patterned lithographically. Finally, 8 – 10 μm of PMMA will be spun on the front surface of the wafer. An array of 100 μm pillars will be defined on the front surface of the wafer, located at the corners of the membranes etched into the back surface of the wafer.

The top wafer with it's array of nanocomposite strips will then be clamped down onto the array or pillars projecting up from the bottom wafer. The entire assembly should look like Fig. 12, with the PMMA pillars located at the corners of the membranes, defining a 10 μm gap between the two wafers, and the CNT/PMMA nanocomposite strips sitting immediately above the 2μm thick membranes. Since the nanocomposite strips will have been assembled into 3 - 5 μm pits in the oxide, a 3 - 5 μm gap will separate the nanocomposite strips from the membranes on the bottom wafer.

To demonstrate it's operation, the assembled device will be placed under vacuum. Evacuating the gap between the top and bottom wafers will reduce conduction heat transfer across the gas gap to a negligible level. As a result, the effective thermal conductivity of the device, with the nanocomposite strips not in contact with the Si membranes is predicted to be on the order of 0.01 W/mK. The device will then be actuated electrostatically, by applying voltage to the Au electrodes on the top and bottom wafers, and drawing the membranes into contact with the nanocomposite strips. Upon contact, the effective thermal conductivity of the device is predicted to rise to approximately 10 W/mK. The effective thermal conductivity of any membrane-defined thermal element can then be varied between 10^{-2} and 10 W/mK by making or breaking contact between the membrane and the nanocomposite. Effective thermal conductivities anywhere in the range of 10^{-2} to 10 W/mK can be achieved by changing the fraction of time the thermal element is actuated or "on" and taking advantage of the thermal mass of the top Si wafer to time

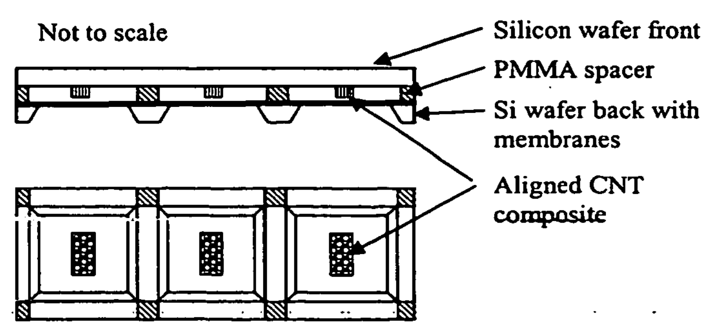

Fig. 10 Prototype thermal switch incorporating aligned CNT composite.

average the instantaneous thermal conductivity. Likewise, by actuating membranes across the array, individual thermal elements can be turned "on" and "off" at will, creating spatially and temporally varying patterns of thermal conductivity. As a result, each membrane then acts as a digital thermal element, much like the more familiar digital picture elements (pixels) found on many display devices.

MANAGEMENT PLAN

To achieve the goals outlined above we have assembled an interdisciplinary team of faculty from mechanical engineering, manufacturing engineering, physics, electrical engineering, and materials science. There are three institutions involved: Washington State University Pullman, WSU/P; Washington State University Vancouver (urban campus), WSU/V; and Portland State University, PSU. WSU/V and PSU are located within a 30 minute drive of each other, while WSU/P is approximately a 8 hour drive from these locations. The team members, their discipline, institution, and primary roles on the project are described below.

- Cecilia Richards: Mechanical Engineering, WSU/P. Professor Richards will act as project manager and provide overall vision and leadership for the team.
- Jun Jiao: Physics, PSU. Professor Jiao will synthesize the CNT's for this work.
- C.-S. "Daniel" Chiang: Manufacturing Engineering, WSU/V. Professor Chiang will characterize the CNT's provided by PSU with scanning probe microscopy.
- Robert Richards: Mechanical Engineering WSU/P. Professor Richards will design and analyze the composite structures and devices.
- David Bahr: Materials Science WSU/P. Professor Bahr will fabricate and characterize the composite structures.
- Mohamed Osman: Electrical Engineering WSU/P. Professor Osman will model thermal properties of the CNT's.
- Sinisa Mesorovic: Mechanical Engineering, WSU/P. Professor Mesorovic will model mechanical properties of the CNT's.

WSU/P will be the lead institution in this work and will provide overall project management on the technical and business levels. Professor Cecilia Richards has experience in managing research projects that span disciplines and institutions. She has been the project manager for two large multi-institution and interdisciplinary programs with WSU as the lead.

Because this is an interdisciplinary and multi institution project teaming strategy is important to the success of the work. First the long term goal of the each team member is to contribute to the common goal of manufacturing a device with a digital thermal conductivity that can be controlled with high resolution both temporally and spatially. Each group will develop short term goals in conjunction with the other groups to ensure compatibility with each other and the long term goal. Adjustments to the short term goals will be directed by results and discovery.

The properties and structure of the CNT's and composite blocks provide focal points for the exchange of information. CNT production at PSU, CNT characterization at WSU/V, CNT modeling and CNT composite characterization and modeling at WSU/P will be tightly coupled together. Information about structure, properties and function at the nanometer scale will be combined and compared with similar information gathered at the micrometer scale and used to guide CNT production as well as CNT composite fabrication

Researchers will meet in person on a quarterly basis to discuss issues and plan short term research goals. A website for the dissemination of research results will be developed so that students and faculty will have quick access to results important to their tasks. To ensure interaction between researchers and communication of important results and requirements each group will regularly provide feedback to the others in monthly reports and phone conferences. In addition, all students

working on the project will submit weekly progress reports. These progress reports will be posted on the website so that all members of the team can access them.

In addition to regularly scheduled interactions between faculty participants an informal exchange program for graduate and undergraduate students will be implemented. Students will travel to each of the sites for a period of 1 to 2 weeks during the summer session to learn about the activities of the other institutions. This will provide the students with an overall view of the project and be an enrichment experience for their studies. During each summer a larger group seminar, in which all students present their work to the faculty and other students will be held during the exchange period that summer.

EDUCATION AND OUTREACH PLAN

The educational plan is a key part of this proposal. Our educational plan will target undergraduate recruitment and retention, and enhance undergraduate/graduate curricula in areas related to this research. In addition, we will use this research as a basis for developing an outreach program to K-12 and community college teachers.

We have requested funding for five graduate students and several undergraduate students for each year of this project. In addition, the School of Mechanical and Materials Engineering has agreed to provide support for an additional two graduate students for each year of the project (a letter of support is attached). With the established REU site programs focused on characterization at both PSU and WSU, four students (2 from each campus) will be selected each year to participate on this collaborative effort. The PI's have found that characterization projects are particularly suitable REU projects, where students ranging from freshmen to seniors can get hands on experience working on experimental methods, and accomplish enough in the span of one summer to merit publication in journals or presentation at regional, national, and international conferences. Obvious characterization related projects for this proposal include TEM and AFM characterization of nanotubes, SEM investigation of patterned structures, mechanical properties measurements using the new instrumentation described in this proposal, and structural characterization of composites at all stages of processing textured nanotube composite structures using TEM and SEM. Professors Jiao and Bahr plan to continue their commitment to targeting female and minority undergraduate students. In the next four years, it is estimated that 12 REU students will be trained through this proposed research, in addition to the seven graduate students in physics, mechanical engineering, manufacturing engineering, and materials science.

WSU/V is hosting a summer workshop of engineering and science for the faculty of local community colleges, and the teachers and students of local high schools. The proposed research will serve as one of the modules of learning and outreach for this summer workshop.

As part of the outreach effort of this project we will develop a workshop series to be targeted at three different audiences; the student and faculty participants directly involved in the research, interested students or faculty at the participating institutions, and community college and high school teachers in the greater Portland-Vancouver area. Each participating institution will develop a workshop module focused on their contribution to the project, that is, PSU will develop a module on carbon nanotube synthesis, WSU/V on their characterization, and WSU/P on their incorporation in a MEMS scale device. Each summer the workshop series will be given at the urban campuses to reach as many teachers as possible. The urban location chosen, the Portland OR – Vancouver WA region, is central to the northwest population density, and should be able to attract teachers from a wide demographic cross section, including teachers from Native American reservations.

We have budgeted money to pay area high school and community college teachers a reasonable stipend and travel expenses and housing (if needed for teachers from more than a 1 hour drive) for their attendance at the 2 day workshop. We choose the model of a short, intensive workshop as the best means to attract participants who have a wide variety of previously scheduled commitments

during the summer. Previous experience has shown that reaching out to a large number of faculty during the summer seems to have the most success attracting a diverse group, rather than concentrating on only certain local schools. We have budgeted enough to cover expenses for 10 teachers to participate each year. A typical 2 day workshop would cover a tour of the synthesis lab and electron microscopy facilities in the morning, along with presentations of the types of material that can be grown and examined with these techniques. After lunch, a demonstration of the electron microscopy facilities (hands on) of both SEM and TEM will be shown to the teachers. The second day would move to the WSU/V campus, and tour the scanning probe facilities in the morning. Afternoon, the WSU/P group would provide mobile demonstration setups of hands on systems for workshop participants to see real multiscale devices and go through the clean room on the WSU/V campus for participants to experience the environment of MEMS, NEMS, and microelectronics fabrication.

Both WSU and PSU have a good track record in attracting under represented groups to our research teams. At WSU we have consciously created a culture that students vie to be a part of and as a consequence we attract the best from all groups. In the past years we have been successful in recruiting and graduating female students, students of Hispanic heritage, an African American student, a Native American student, and an MS student who was the first in his family to graduate from college.

At PSU, Prof. Jiao also plans to extend outreach activities to female high school students and to foster their interest in math- and science-based careers. Prof. Jiao plans the following specific activities which couple well with her location in an urban environment:

- Arrange an annual open house for the girl scouts and girls' clubs from the Portland area to tour our research laboratories and offer them seminars, which highlight the research work of women at universities nationwide.
- Recruit two highly motivated female students from local high schools, allowing them to participate in the summer research in Prof. Jiao's group.
- Continue the collaborations with Portland High School District's Talented and Gifted Student Program, Oregon Museum of Science and Industry's Science Education Resource Center, and the Saturday Academy of Oregon's high school student Apprenticeships in Science and Engineering Program. Serve as a mentor and advisor in these programs.

BROADER IMPACTS

As described above we are committed to using our research to promoting teaching, training, and learning. We all participate in activities targeted not only at graduate students but also undergraduates, under represented groups, K-12, and teachers. Both WSU and PSU have a good track record in attracting under represented groups to our research teams. We recognize the need to target members of underrepresented groups early to stimulate them to be interested in science and engineering. As outlined above we have several activities planned which address this need.

This project will enhance infrastructure for research and education in the northwest and nationally. On the national scale this research will lead to the development of a new class of devices with application in all sectors of society. The research will also lead to the development of next-generation equipment which will enhance research opportunities for others in this field of research. To perform simultaneous testing of thermal and mechanical properties of nanostructures a novel device will be constructed, allowing unique measurement capabilities of what we perceive as the next frontier in bringing nanoscale structures from the lab to engineered devices. Without demonstrating the capabilities of this type of instrumentation in a research environment, it is highly unlikely that commercial suppliers will be interested in developing systems to deliver to the large number of researchers we feel will soon (2-5 years) be working on these scales (nm to mm).

On the regional scale the project greatly enhances interactions between urban campuses geared for liberal education (PSU), urban branch campuses of a multi-campus system (WSU/V) serving many non-traditional students, and a traditional rural research university (WSU/P). This work provides research interactions between students at these schools and opportunities to target groups traditionally under-represented in STEM programs. Possible collaborative efforts with the carbon nanotube growth group at Pacific Northwest National Laboratory is another area where the impact between all three campuses and the regional national laboratory can be strengthened.

We have several activities planned to provide a broad dissemination of our work to enhance scientific understanding of the "nano world" for the general lay public. We feel that this is an especially important task in a time when the general public is highly suspicious of nanotechnology. We feel that our work can provide a concrete example of how nano technology can be used for beneficial means. To that end we have planned the following:

- As part of this project we will develop a website for the general public about carbon nanotubes – how to make them, their properties, and their uses.
- Collaborations with Portland High School District, the Oregon Museum of Science and Industry will lead to direct exposure to K-12 students in the region.
- By involving K-12 and community college teachers in the summer workshop series we hope to help them develop material for their classrooms and arrange for "field trips' to our labs. We will provide presentations, samples, and demonstrations in conjunction with input from the teachers at the workshops to help them bring nanoscience and technology to their classrooms and students.

RESULTS FROM PRIOR NSF SUPPORT

Robert Richards PI Co PI's: D.F. Bahr, C.D. Richards

DMI #9980837, 'xyz on a Chip' $520,000 8/99 – 9/02

Title: MEMS-Based Power Generation for Portable Systems

The goal of this project has been to design, develop, and demonstrate a highly flexible, highly modular MEMS-based power system. The system demonstrated during the project, dubbed the P^3 micro power generation system, is based on a two-dimensional, modular architecture. A complete power system is built up of individual generic modules or unit cells in which all the functions of an engine are integrated. Each unit cell is an external combustion engine, in which thermal power is converted to mechanical power through the use of a novel thermodynamic cycle that approaches the ideal vapor Carnot cycle. Mechanical power is converted into electrical power through the use of a thin-film piezoelectric (PZT) membrane generator. A power supply can be assembled out of any number of unit cell engines combined together. This modularity gives great flexibility in the assembling of micro power generation systems, first in the power output of a given P^3 power system and second in the range of temperature operation of the system.

The lead institution in this project is Washington State University with Oregon State University a collaborating institution. The primary goal of the project has been to develop and demonstrate a single P^3 micro heat engine (unit cell). Washington State University has now successfully fabricated, tested, and demonstrated first generation prototypes of a single cell P^3 micro engine. Three generations of PZT (Lead Zirconate Titanate) membrane generators, the key component of the engine, have been developed and characterized. The latest generations of piezoelectric membrane generator have been successfully integrated into engines to demonstrate electrical power production by the P^3, the first successful MEMS dynamic heat engine.

To date the work has resulted in 4 archival publications, 17 refereed conference proceedings, and 8 conference papers. There are currently 2 more archival publications in review. Two doctoral students, five M.S. students, and six undergraduates have been supported on this project.

David Bahr PI

NSF # 9876937, REU $168,000, 05/15/99-05/31/02 & NSF # 0139125, $195,000, 05/01/02-04/30/4

These awards cover our REU site "*Characterization of Advanced Materials*" at Washington State University (WSU). Our target population for REU program participants was primarily from schools from the Pacific Northwest and Rocky Mountain states that do not have access to the modern instrumentation that is needed for materials research or do not have specific MSE programs. We aimed to provide students, both from institutions with limited research programs as well as students from groups traditionally underrepresented in science and engineering, a 10 week experience that would stimulate their interest in materials science while providing them with technical skills for their future careers. We placed particular emphasis on attracting students from demographic groups traditionally underrepresented in engineering, particularly women. Additionally, we strove to attract students from a variety of majors into materials research, and to reach students of all ages (freshmen to seniors).

In this program we have attracted 55 participants from 21 different schools and from 14 different states. Women account for 45% of the participants. To date, all of the program participants who have graduated are either in graduate school or are in an industry engineering job. To date, 21 publications or presentations with REU undergraduates (with three more currently in progress from this past summer) have been generated.

Cecilia Richards PI

CTS-9457108 NSF Young Investigator Award $335,000 9/94 – 3/00

NSF NYI funds were used to support two research thrusts: 1) the dynamics of droplet-vortex interactions in nonreacting and reacting jets, and 2) the development of a technique to measure temperature on the microscale. An experimental study of the role of large-scale structures in droplet and vapor transport in droplet-laden jets was conducted. The results show that injection location has a substantial impact on both droplet and vapor convection. Droplets must directly interact with large-scale structures to realize a significant increase in dispersion. In a reacting jet the combination of transport effects and droplet evaporation leads to the formation of droplet clusters. The group combustion behavior of the droplet field was evaluated by estimating the group combustion number from experimental data. The use of thermochromic liquid crystals as a micro temperature probe was developed for studies of fundamental droplet heat transfer. Microencapsulated beads of thermochromic liquid crystals were doped into droplets exposed to convective cooling and heating. The technique has the potential to extend to MEMS devices. Temperature measurements with a spatial resolution of 5 microns are possible. Work from this award has resulted in six journal publications, eight refereed conference papers, and 12 conference papers. A best paper award was received in 1996 for the work on nonreacting jets. Two postdoctoral researchers, one PhD student, five MS students, and four undergraduates were supported.

Jun Jiao: PI

NSF# ECS-021706 $180,000 1 /15/2002 – 6/30/2005

Title: Integration of Nanoscience and Nanotechnology Research, Education, and Outreach: Systematic Tailoring of Carbon Nanotubes to Designed Electronic Properties

The overall effort of this project is to develop an integrated research, education, and outreach program in nanoscience and technology at Portland State University (PSU), with an emphasis on carbon nanotube research. A novel technique developed was the position-controlled growth of carbon nanotubes by a combination of focused ion beam and chemical vapor deposition. This has allowed us to localize catalytic components in selected areas, enabling the growth of carbon nanotubes on sharp

tips. As a result, we can investigate the electron field emission behavior of an individual carbon nanotube in relation to its geometrical configuration and the applied field. The study of the angular distribution of the electron beam emitted from a single carbon nanotube helped us understand the still unidentified electronic properties of individual carbon nanotubes. Broader impacts of this research included training graduate students, mentoring five REU students, and involving two local high school students.

NSF# DMR – 0097575 $189,000 6/1/2001 – 5/31/2004
REU Site: Applications of Microscopy and Microanalysis to Multidisciplinary Research

This is the first NSF sponsored REU site at Portland State University (PSU) and the first one in the Portland metropolitan area. The objective of this program is to inspire undergraduate students – with emphasis on women and minorities – to pursue careers in science and engineering by involving them in "real-life" research. A major effort of this REU program is to create opportunities for highly motivated, underrepresented undergraduate students early in their education to do independent research in faculty laboratories. This REU site also serves as a magnet bringing together undergraduate students from different disciplines, ethnic backgrounds, and from institutions where research opportunities are limited. The REU site is composed of a summer program and a year-round component. More than a dozen REU participants have presented their research findings in the Pacific Northwest Conference of the American Vacuum Society, and the Northwest Undergraduate Science Research Conference. Two of them won the first place undergraduate awards consecutively in the last two years. To date, there are more than two-dozen publications and conference presentations carrying the acknowledgment of this NSF award and more then a dozen refereed publications in which the REU participants served as co-authors.

References

1. A. Miner, A. Majumdar and U. Ghoshal, "Thermomechanical refrigeration based on transient thermoelectric effects," *Applied Physics Letters*, **75**, 1176-1178, (1999)
2. G. J. Snyder, J-P. Fleurial, T. Caillat, R. Yang and G.Chen, "Supercooling of Peltier cooler using a current pulse," *Journal of Applied Physics*, **92**, 1564-1569, (2002)
3. C.T. Wittwer, G.C. Fillmore and D.J. Garling, "Minimizing the time required for DNA amplification by efficient heat transfer to small samples," *Anal. Biochem.*, **186**, 328-331, (1990)
4. S.T. Tan and J.H. Weiss, "Development of a sensitive reverse transcriptase PCR assay, RT-PCR, utilizing rapid cycle times," *PCR Methods Appl.* **2**, 137-143, (1992)
5. J. Khandurina, T.E. McKnight, S.C. Jacobson, L.C. Waters, R.S. Foote and J.M. Ramsey, "Integrated system for rapid PCR-based DNA analysis in microfluidic devices," *Anal. Chem.*, **72**, 2995-3000, (2000)
6. B.C. Giordano, J. Ferrance, S. Swedberg, A.F.R Huhmer and J.P. Landers, "Poymerase chain reaction in polymeric microchips: DNA amplification in less than 240 seconds," *Anal. Biochem*, **291**, 124-132, (2001)
7. S. Whalen, M. Thompson, D. Bahr, C. Richards and R. Richards, "Design fabrication and testing of the P3 micro heat engine" *Sensors & Actuators: A. Physical*, **104**, 200-208 (2003).
8. A.O. Christensen, J.P. Jacob, C.D. Richards, D.F. Bahr and R.F. Richards, "Fabrication and Characterization of a Liquid-Metal Micro-Droplet Thermal Switch," *Proceedings of Transducers '03*, Paper No. AM069, Boston, (2003)
9. A.O. Christensen, J.P. Jacob, C.D. Richards, D.F. Bahr and R.F. Richards, "Fabrication and Characterization of a Liquid-Metal Micro-Droplet Array for Use as a Thermal Switch," *Proceedings of ASME HT2003*, Paper No. HT2003-40317, (2003).
10. P. Kim, L. Shi, A. Majumdar and P.L. McEuen, "Thermal transport measurements of individual mulitwalled nanotubes," *Physical Review Letters*, **87**, 215502, (2001).
11. J. Hone, M. Whitney, C. Piskoti and A. Zettl, "Thermal conductivity of single-walled carbon nanotubes," *Physical Review B*, **59**, R2514-R2516, (1999).
12. W. Yi, L. Lu, Zhang Dian-lin, Z.W. Pan and S.S. Xie, "Linear specific heat of carbon nanotubes," *Physical Review B*, **59**, R9015-R9018, (1999).
13. J.E. Fischer, W. Zhou, J. Vavro, M.C. Llaguno, C. Guthy, R. Haggenmueller, M.J. Casavant, D.E. Walters and R.E. Smalley, "Magnetically aligned single wall carbon nanotube films: preferred orientation and anisotropic transport properties," *Journal of Applied Physics*, **93**, 2157-2163, (2003).
14. M.J. Biercuk, M.C. Llaguno, M. Radosavljevic, J.K. Hyun and A.T. Johnson, "Carbon nanotubes composites for thermal management," *Applied Physics Letters*, **80**, 2767-2769, (2002).
15. R. Haggenmueller, H.H. Gommans, A.G. Rinzler, J.E. Fischer, K.I. Winery, "Aligned single-wall carbon nanotubes in composites by melt processing methods," *Chemical Physics Letters*, **330**, 219-225, (2000).
16. D.G. Cahill, W.K. Ford, K.E. Goodson, G.D. Mahan, A. Majumdar, H.J. Maris, R.Merlin and S.R. Phillpot, 'Nanoscale Thermal Transport,' *Applied Physics Reviews*, **93**, 793-818, (2003).
17. T.W. Odom, J.L. Huang, P. Kim, C.M. Lieber, "Atomic structure and electronic properties of single-walled carbon nanotubes ", *Nature* **391**, 62-64 (1998)

18. J.W.G. Wildoer, L.C. Venema, A.G. Rinzler, R.E. Smalley, "Electronic structure of atomically resolved carbon nanotubes", *Nature* **391** 59-61 (1998)
19. E. Oesterschulze, M. Stopka, L. Ackermann, W. Scholz, S. Werner, "Thermal imaging of thin films by scanning thermal microscope", *J. Vac. Sci. Technol. B* **14**, 832-837 (1996)
20. E.W. Wong, P.E. Sheehan, C.M. Lieber, "Nanobeam Mechanics: Elasticity, Strength, and Toughness of Nanorods and Nanotubes", *Science* **277**, 1971-1975 (1997)
21. D.A. Walters, L.M. Ericson, M.J. Casavant, J. Liu, K.A. Smalley, "Elastic strain of freely suspended single-wall carbon nanotube ropes", *Appl. Phys. Lett.* **74**, 3803-3805 (1999)
22. Wen, J.G.; Huang, Z.P.; Wang, D.Z.; Chen, J.H.; Yang, S.X.; Ren, Z.F.; Wang, J.H.; Calvet, L.E.; Chen, J.; Klemic, J.F.; Reed, M.A. "Growth and characterization of aligned carbon nanotubes from patterned nickel nanodots and uniform thin films" *J. Materials Research*, **16**, p 3246-3253 (2001).
23. Choi, G.S. ; Cho, Y.S.; Son, K.H.; Kim, D.J. "Mass production of carbon nanotubes using spin-coating of nanoparticles" *Microelectronic Engineering*, **66**, 77-82 (2003).
24. Ph. Mauron., Emmenegger, Ch.; Zuttel, A.; Nutzenadel, Ch.; Sudan, P.; Schlapbach, L.; "Synthesis of oriented nanotube films by chemical vapor deposition" *Carbon*, **40**, 1339-1344 (2002)
25. Sennett, M. ; Welsh, E.; Wright, J.B.; Li, W.Z.; Wen, J.G.; Ren, Z.F. "Dispersion and alignment of carbon nanotubes in polycarbonate"*Applied Physics A: Materials Science and Processing*, **76**, 111-113 (2003).
26. Thostenson, Erik T. ; Chou, Tsu-Wei "Aligned multi-walled carbon nanotube-reinforced composites: Processing and mechanical characterization" *Journal of Physics D: Applied Physics*, **35**, L77-L80 (2002).
27. Stephan, Christophe ; Nguyen, Thien Phap; Lahr, Bernd; Blau, Werner; Lefrant, Serge; Chauvet, Olivier "Raman spectroscopy and conductivity measurements on polymer-multiwalled carbon nanotubes composites" *Journal of Materials Research*, **17**, 396-400 (2002).
28. Park, Cheol ; Ounaies, Zoubeida; Watson, Kent A.; Pawlowski, Kristin; Lowther, Sharon E.; Connell, John W.; Siochi, Emilie J.; Harrison, Joycelyn S.; St. Clair, Terry L. "Polymer-single wall carbon nanotube composites for potential spacecraft applications" *Materials Research Society Symposium - Proceedings*, **706**, 91-96 (2002).
29. M. Pang and D.F. Bahr, "Thin Film Fracture During Nanoindentation Of A Titanium Oxide Film – Titanium System" Journal of Materials Research, **16**, 2634-2643 (2001)
30. Volinsky, A.A. ;Moody, N.R.; Gerberich, W.W., "Interfacial toughness measurements for thin films on substrates" *Acta Materialia*, **50**, 441-466 (2002).
31. Bahr, D.F. , Hoehn, J.W.; Moody, N.R.; Gerberich, W.W. "Adhesion and acoustic emission analysis of failures in nitride films with a metal interlayer" *Acta Materialia*, **45**, 5163-5175 (1997).
32. Bernholtz, J., Brenner, D., Buongiorno Nardelli, M., Meunier, V. & Roland C. "Mechanical and electrical properties of nanotubes" *Annu. Rev. Mater. Res.* **32**, 347-375 (2002).
33. L. X. Benedict, S. G. Louie, and M. L. Cohen, "Heat Capacity of carbon nanotubes," *Solid State Commun.* **100**, 177-180 (1996).
34. W.E. Picket, J.L. Feldman and J. Deppe, "Thermal transport across boundaries in diamond structure materials," *Modeling Simul. Mater. Sci. Eng.* **4**, 409-419 (1996).

35. M. A. Osman and D. Srivastava,'Temperature dependence of the thermal conductivity of single wall carbon nanotubes," *Nanotechnology* **12,** 21-24 (2001).
36. J Tersoff, "Empirical Interatomic Potential for Carbon, with Applications to Amorphous Carbon, " *Physical Review Letters* **61,** 2879-2882 (1988).
37. D. W. Brenner,"Empirical potential for hydrocarbons for use in simulating the chemical vapor deposition of diamond films," *Physical Review B* **42,** 9458-9471 (1990).
38. J Che, T Cagin and W A Goddard III,"Thermal Conductivity of Carbon Nanotubes," *Nanotechnology* **11,** 65-69 (2000).
39. C Oligschleger and J C Schön, "Simulation of thermal conductivity and heat transport in solids," *Physical Review B* **59,** 4125-4133 (1999).
40. S. Motoyama, Y. Ichikawa, Y. Hiwatari and A. Oe,"Thermal Conductivity of unranium dioxide by nonequilibrium molecular dynamics simulations, *Physical Review B* **60,** 292-298 (1999).
41. Yakobson B.I., Brabes, C.J. & Bernholc, J. "Nanomechanics of carbon tubes: Instabilities beyond linear response", *Phys. Rev. Letters* **76,** 2511-2514 (1996).
42. Iijima, S., Brabec, C., Maiti, A. & Bernholc, J. "Structural flexibility of carbon nanotubes", *J. Chem. Physics* **104,** 2089-2092 (1996).
43. Brenner D.W., Harrison, J.A., White, C.T. & Colton, R.J. "Molecular dynamics simulations of the nanometer-scale mechanical properties of compressed Buckminsterfullerene", *Thin Solid Films*, **206**, 220-223 (1991).
44. Falvo M.R., Clary, G.J., Taylor R.M. II, Chi, V., Brooks, F.P. Jr., Washburn, S. & Superfine, R. "Bending and buckling of carbon nanotubes under large strain", *Nature* **389**, 582-584 (1997).
45. Buongiorno Nardelli M., Yakobson, B.I. & Bernholc, J. "Brittle and ductile behavior in carbon nanotubes", *Phys. Rev. Letters* **81**, 4656-4659 (1998).
46. Zhao Q., Buongiorno Nardelli M. & Bernholc, J. "Ultimate strength of carbon nanotubes: A theoretical study", *Phys. Rev. B* **65**, 144-155 (2002).
47. Srivastava, D., Menon, M. & Cho, K. "Nanoplasticity of single-wall carbon nanotubes under uniaxial compression", *Phys. Rev. Letters* **83**, 2973-2976 (1999).
48. Tombler T.W., Zhou, C., Alexseyev, L., Kong, J., Dai, H., Liu, L., Jayanthi, C.S., Tang, M. & Wu, S-Y. "Reversible electromechanical characteristics of carbon nanotubes under local-probe manipulation", *Nature* **405**, 769-772 (2000).
49. Koiter, W.T. "On the nonlinear theory of thin elastic shells". *Proc. Kon. Ned. Ak. Wet.* **B69**, 1-54 (1966).
50. Niordson, F.I. *Shell Theory* North-Holland series Appl. Math. Mech. Vol. 29. (1985)
51. Libai A. & Simmonds, J.G. *The nonlinear theory of elastic shells.* Cambridge University Press, Cambridge, UK (1988).
52. Hughes, T.J.R. *The Finite Element Method.* Dover, NY (2000).
53. Tvergaard, V. & Needleman, A. "Buckling localization in a cylindrical panel under axial compression", *Int. J. Solids Structures* **37**, 6825-6842 (2000).
54. Strandman C, Backlund Y "Bulk silicon holding structures for mounting of optical fibers in V-grooves", *J Microelectromech Systems* **6**, 35-40 (1997)
55. Uthara Srinivasan, Michael A. Helmbrecht, Christian Rembe, Richard S. Muller, and Roger T. Howe, "Fluidic Self-Assembly of Micromirrors Onto Microactuators Using Capillary Forces" IEEE Journal On Selected Topics In Quantum Electronics, **8**, 4-12 (2002).

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